FINAL REPORT

Technical Feasibility Study of an Effective Low-toxicity Obscurant Material

SERDP Project WP-2148

AUGUST 2012

Rutger Webb
TNO

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
15-08-2012

2. REPORT TYPE
FINAL

3. DATES COVERED *(From - To)*
04/2011 – 07/2012

4. TITLE AND SUBTITLE

Technical feasibility study of an effective low-toxicity obscurant material

5a. CONTRACT NUMBER
W912HQ-11-C-0034

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Webb, Rutger
Ramlal, Dinesh, R.
Langenberg, Jan. P.
Alblas, Marcel. J.

5d. PROJECT NUMBER
WP-2148

5e. TASK NUMBER

5f. WORK UNIT NUMBER
032.31738

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

TNO
Department of Energetic Materials,
Lange Kleiweg 137
2288 GJ Rijswijk
The Netherlands

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
SERDP & ESTCP Program Offices
901 North Stuart Street, Suite 303
Arlington, VA 22203-1853

10. SPONSOR/MONITOR'S ACRONYM(S)

SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The composition made were containing various amounts of $NaClO_3$, cellulose, $CaCO_3$ and Mg (from two different sources). From the laboratory scaled tests the composition named "11EM0745" was are the best performing composition made. When these compositions are compared to the benchmark obscurant compositions (HC smoke, red phosphorus smoke, and TPA smoke) it is concluded that the transmissions through the smoke of the new see-salt compositions are much higher compared to the HC and RP smoke, but lower compared to the TPA smoke. The smoke from developed compositions are less toxic than the HC, RP and TPA smokes.

15. SUBJECT TERMS obscurant smoke, pyrotechnic composition, new pyrotechnic composition formulation, safety study, transmission measurements, effectiveness, in vitro toxicity screening, Cultex, sea salt aerosol, electron microscope

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON : Mr. R. Webb
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
Unclass.	Unclassified	Unclassified	None	47	+31 88 86 61449

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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List of Acronyms

ASTM	American Society for Testing and Materials
BAM	Bundesanstalrt fuer Materialuntersuchung
Calspan	Calspan Advanced Technology Center, of Calspan Corporation
CEA	Chemical Equilibrium with Applications, a NASA thermodynamic code
Cultex®	Platform for the in-vitro toxicological analysis of airborne substances
GAD	Gaseous Analytical Detector
HaCaT	human keratinocytes; cells on the outermost layer of the skin
HC smoke	Smoke composition comprising a significant percentage hexachloroethane
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
KM smoke	Patented smoke; name derived from initials of Potassium and Magnesium
LDH	Lactate dehydrogenase
LS-1	Light source (tungsten halogen) of Ocean Optics Inc.
MTT	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide
PM_{10}	Particle matter 10 µm
$PM_{2.5}$	Particle matter 2.5 µm
PVA	Polyvinyl alcohol
RDX	Hexogen; cyclo-1,3,5,trimethylene-2,4,6-trinitramine
RP	Red Phosphorus
RP smoke	Smoke composition comprising in large part RP
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
SEM	Scanning Electron Microscope
TNO	Netherlands Organization for Applied Scientific Research
TPA smoke	Smoke composition comprising a significant percentage terephthalic acid
UK	United Kingdom
WP	Weapon Platforms

Keywords
Sea-salt based composition, low-toxicity, obscurant smoke

Acknowledgements
The authors wish to gratefully acknowledge the financial support by the Weapon Systems and Platforms (WP) section of the Strategic Environmental Research and Development Program (SERDP) of this project, WP-2148.

Executive Summary

The objective of this SERDP Exploratory Development (SEED) project is to investigate the technical feasibility of developing a new pyrotechnic obscurant material based on ingredients that are environmentally benign. Furthermore, during functioning the material should generate a combustion product (smoke) that is low in toxicity.

The focus in this SERDP effort is the use of a sea-salt based smoke generating obscurant with a low toxicity for flora and fauna. This research contains four main activities:

- A desk study to be able to choose a limited number of sea-salt based components and rank them according to low toxicity, low ecotocology, low persistence, low bioaccumulation and hygroscopic

- Select various base compositions containing the chosen components

- Perform labscale testing to obtain information about the safety (friction and impact), the smoke formation (transmission), the formed particle size and particle size distribution and toxicity (by in vitro testing)

- The proof of concept. A scaled down version of a hand grenade with the most promising composition was and tested on a proofing ground

The compositions made contained various amounts of sodium chlorate, cellulose, calcium carbonate and magnesium (from two different sources). From the laboratory scaled tests the composition named “11EM0745” was the best performing composition. When these compositions are compared to the benchmark obscurant compositions (hexachloroethane smoke, red phosphorus (RP) smoke, and terephthalic acid based smoke) it is concluded that the transmissions through the sea-salt compositions are much higher compared to the hexachloroethane smoke and RP smoke, but lower compared to the terephthalic acid based smoke. The smoke from developed compositions are less toxic than the hexachloroethane, RP and terephthalic acid smokes. Furthermore the ingredients used are easy to obtain and low in costs.

With these results in mind, it seems feasible to obtain a less toxic smoke forming composition based on composition 11EM0745. However some fine tuning is needed to further reduce the transmission of the smoke. This report contains an outline of potential next steps for a follow on research.

1 Introduction

Objective
Military obscurants exist as handheld devices (hand grenades) but are also frequently used in the form of mortar and artillery rounds. Besides the fact that these obscuration munitions pose a toxicity hazard to the user, the environmental impact of these munitions can also be significant (e.g., the use of hexachloroethane (HC)). On the other hand, handheld obscurants are today still very important munitions for the protection of war fighters, allowing their concealment at frontlines.
The objective of this SERDP Exploratory Development (SEED) project is to investigate the technical feasibility of developing a new pyrotechnic obscurant composition based on ingredients that are environmentally benign. Furthermore, during functioning the material should generate a combustion product (smoke) that is low in toxicity.

Background
Pyrotechnic (white) obscurant munitions are being used for obscuration in training and in real operations on the battlefield. In the past, HC smoke was very much in demand as white obscurant to create dense white smoke screens on the battlefield. HC smoke is a highly effective obscurant comprising hexachloroethane (C_2Cl_6) and zinc oxide (ZnO).
These ingredients form combustion products through a strongly exothermic reaction. Said combustion products consist of a dense cloud of very small zinc chloride particles and hydrochloric acid, which altogether makes it a toxic obscurant. (Leenders, 1996) The typical size of these obscurant particles is in the range of submicron to a few microns. Furthermore these particles are hygroscopic, which causes these particles to grow, and thus also lead to a favorable 'yield factor' of the obscurant munitions.
Hexachloroethane is found to be possibly carcinogenic to humans.

Prior knowledge
Two strands of research are significant for this report namely:

(I) The development of the Potassium Magnesium (KM) Smoke by the late Dr. Krone of the former NICO Pyrotechnik, now known as part of Rheinmetall Weapons & Munitions. (Krone 1985/1989/1990/2009). KM Smoke consists of a pyrotechnic obscurant composition comprising magnesium, potassium nitrate and potassium perchlorate. The combustion reaction has been described by Dr. Krone as the following chemical equation:

$$9\ Mg + 2\ KNO_3 + KClO_4 \rightarrow 9\ MgO + K_2O + KCl + N_2 + \text{Energy}$$

To make good use of the excess energy, around 44% of potassium chloride (KCl) is being dispersed from this composition.

(II) The development of "Salty Dog" and "Salty Frog" and similar compositions. This is an effort sponsored by the Naval Air Systems Command, and amongst others subcontracted to Calspan. The concept is a so called 'hygroscopic aerosol smoke'. Here small amounts of lithium salts are used for its hygroscopic character to attract water so it can generate large particles. (Hanley, 1980/1981/1983/1985). In Table 1.1 some examples of compositions studied are listed.

Table 1.1 Compositions based on the use of hygroscopic lithium-salts (Blomerth, Hanley).

	558 "Salty Dog"	CY85A "Salty Frog"	CY91 "Salty Frog II"	NWC 29	NWC 78	NWC 79	NWC 90	NWC 164
Potassium perchlorate	61	65	24	-	25	29	23	22
Ammonium perchlorate	-	-	17	-	-	-	-	-
Sodium perchlorate	-	-	-	79	54	40	46	45
Sodium chloride	17	10	30	-	-	10	-	-
Lithium chloride	-	-		2	2	2	2	2
Lithium carbonate	1	2		-	-	-	-	-
Graphite	-	-		-	-	-	10	10
Magnesium	5	5		5	5	5	5	5
Hydrocarbon binder	18	18		14	14	14	14	16

Approach
Within the TNO Pyrotechnics Laboratory of the department of Energetic Materials, a large number of different pyrotechnic formulations have been studied over the years. During the combustion of some of these formulations, it was observed that they generate an significant amount of smoke. This information was taken into account at the time of the development of the idea to make a sea-salt aerosol based obscurant. It seemed worth the effort to investigate the potential of a sodium chlorate based composition.

This research can be divided into four main activities, namely:

- Choose a limited number of the best sea-salt based components and rank them according low toxicity, low ecotoxicology, low persistence, low bioaccumulation and hygroscopic, based on a desk study.

- Select various base compositions containing the chosen components

- Perform laboratory scale test to obtain information about the safety (friction and impact), the smoke formation (transmission), the formed particle size and particle size distribution and toxicity (by *in vitro* testing)

- The proof of concept. A scaled down version of a hand grenade with the most promising composition was tested on a proofing ground

2. Work Package 1 – Selection of best candidate ‘Obscurant Aerosol Particulate’

In this work package a selection has been made of best candidate ‘Obscurant Aerosol Particulate’. The strategy was to select the “most favorable” chemical from a toxicological standpoint and also with the most “environmentally benign” properties, with the environmental and human health aspects and criteria in mind (as mentioned in ASTM E2552). At the end of this work package the TNO team will select the ‘Obscurant Aerosol Particulate’.

2.1 Criteria used for selection

- Low toxicity (no evidence of carcinogenicity and/or mutagenicity)
- Low ecotoxicity
- Low persistence
- Low bio-accumulation (preferably a naturally occurring)
- Hygroscopic

It is well understood that hygroscopic obscurant aerosol particles are preferred. The effect of hygroscopic growth by obscurant particles is described by, amongst others, the Hänel growth factor. (Accetta, 1993) This growth factor is named after the research done by Gottfried Hänel on the properties of atmospheric aerosol particles as function of the relative humidity at thermodynamic equilibrium with the surrounding moist air. In his research Hänel also confirms that sea salt aerosol is known to be hygroscopic. (Hänel, 1976)
Multiple independent sources have stated that sea salt aerosol has been described as being hygroscopic. (See for example also Chuang, 2000, Tang, 1997, Irshad, 2008)

2.2 Candidate ‘Obscurant Aerosol Particulates’ similar to sea-salt

The list of candidates had been defined and inspired by the notion of generating *in situ* sea-salt. Sea-salt aerosol is primarily composed of the following ions, listed in order of descending abundance by weight:

Chloride (Cl^-)	55.0%
Sodium (Na^+)	30.6%
Sulfate (SO_4^{2-})	7.7%
Magnesium (Mg^{2+})	3.7%
Calcium (Ca^{2+})	1.2%
Potassium (K^+)	1.1%
Bicarbonate (HCO_3^-)	0.4%

Sea-salt aerosol is (not surprisingly) a naturally occurring aerosol. It is well characterized by environmental researchers and it is regarded as a harmless background level in discussions about the PM_{10} and $PM_{2.5}$ and manmade sources. The contribution of sea salt to PM_{10} and $PM_{2.5}$ in the Netherlands is well investigated (Manders, 2009)

TNO’s idea is to generate directly from an exothermic reaction a very fine cloud of obscurant smoke which is very similar in terms of its chemistry to sea-salt aerosol.

The major component of sea-salt is sodium chloride. Sodium chloride can be very simply generated by the combustion reaction of a sodium chlorate based pyrotechnic composition, combined with many organic fuels. For example, using cellulose as the fuel, an unbalanced chemical combustion reaction would be:

$$NaClO_3 + C_6H_{10}O_5 \rightarrow NaCl + CO_2 + H_2O$$

The stoichiometric ratios can be determined by using the oxygen balance values. Doing so yields the following stoichiometric ratio for cellulose and sodium chlorate is 72.42% $NaClO_3$ and 27.58% cellulose.

Since sea-salt is not 100% sodium chloride, and since it is desirable for a pyrotechnic formulator to have some room for optimization, TNO also identified other candidate 'Obscurant Aerosol Particulates'. An example of this is the use of metallic magnesium. Metallic magnesium can in this composition be used to 'tweak' the combustion temperature.

The authors came up with the following list of candidate obscurant particulates which are 'compliant' with the list of requirements:

- Chlorides of sodium, potassium, and ammonium
- Carbonates of magnesium and calcium
- Oxides of magnesium
- Sulfates of magnesium and calcium

3 Work Package 2 – Select best candidate 'Base Composition'

3.1 Materials

The basis composition used for further investigation (Table 3.1) will be a combination of sodium chlorate ($NaClO_3$) with a simple hydrocarbon fuel (cellulose), a metallic Magnesium (Mg) fuel and Calcium Carbonate ($CaCO_3$). The sodium chlorate decomposes under the release of oxygen which will serve for the oxidation of the fuel(cellulose and magnesium). The decomposing residue of sodium chlorate is sodium chloride, which will be the main component in the sea salt based obscurant smoke.
The added cellulose has an important function in generating (carrier) gas during the combustion, however it does not contribute to the formation of a obscurant smoke itself.
The calcium carbonate is added to form cations to mimic the sea salt composition and due its potential to slow down the linear burn rate which is very helpful during the design of full hand grenade items.
The last ingredient in the list is metallic magnesium which yields a higher flame temperature compared to cellulose. The formed magnesium oxides during combustion of the magnesium contributes to a dense white obscurant smoke.

Table 3.1. Base compositions under investigation in this project.

	11EM0xxx												
Composition (wt%)	*735*	*736*	*737*	*738*	*739*	*740*	*741*	*742*	*743*	*744*	*745*	*746*	*747*
$NaClO_3$	69	69	60	65	70	60	60	65	65	70	70	60	60
Cellulose	23	23	35	30	25	32	32	27	27	22	22	30	30
$CaCO_3$	5	5	5	5	5	5	5	5	5	5	5	5	5
Mg (LNR61)	3	0	0	0	0	3	0	3	0	3	0	5	0
Mg (AZ91D)	0	3	0	0	0	0	3	0	3	0	3	0	5

The ingredients were obtained from three suppliers and provided with an internal TNO code for chemicals from TNO department of Energetic Materials (Table 3.2).
For magnesium it is known that it causes corrosion in pyrotechnic munitions. For this reason a lower corrosion magnesium variant was chosen as an ingredient in the base composition. This type of magnesium powder under the name AZ91D was obtained from Metal Powder Technology Ltd, from the UK and is free from hexavalent chromium.

Table 3.2. Supplier and identification numbers from the ingredients used in base composition

Ingredients	*Supplier*	*TNO identification number**
$NaClO_3$	Sigma Aldrich, Product number 244147, ≥ 99%	PM6492-11
Cellulose	Sigma Aldrich, Product number 310697, powder	PM6703-12
$CaCO_3$	Sigma Aldrich, Product number 310034, 98%	PM6702-12
Mg	Ecka Granules, Austria, LNR61	YP9902-001A
Mg	Metal PowderTechnology Ltd, Birmingham, UK, AZ91D	YP1103-02

**YP= Ypenburg, PM = Prins Maurits Lab (both location from the department of Energetic Materials at TNO)*

3.2 Thermodynamic calculations

Thermodynamic calculations are performed to determine the theoretical adiabatic flame temperature ($T_{adiabatic}$) under equilibrium conditions (Table 3.3). For these thermodynamic calculation the German ICT Code is used. These calculations are using a number of assumptions (constant volume, with a fixed final pressure at 1 bar), which understandably will not be valid in real situations. Calculation of the 'Heat of Explosion' is performed without any estimation. Even with the made assumption, the use of this thermodynamic codes still serves the purpose to determine trends in the theoretical adiabatic flame temperature and/or the formation of combustion species for the comparison of the different compositions.

Table 3.3. Thermodynamic calculations of the adiabatic temperature, oxygen balance and the combustion product under equilibrium conditions.

	11EM0xxx							
Composition (wt%)	*735*	*737*	*738*	*739*	*740*	*742*	*744*	*746*
$NaClO_3$	69	60	65	70	60	65	70	60
Cellulose	23	35	30	25	32	27	22	30
$CaCO_3$	5	5	5	5	5	5	5	5
Mg	3				3	3	3	5
$T_{adiabatic}$ (K)	2591	2225	2487	2473	2499	2618	2572	2622
Oxbal (%)	2%	-14%	-6%	2%	-13%	-5%	4%	-12%
Solids (%)	45%	35%	38%	41%	40%	43%	46%	44%

Note: composition 735 is comparable with composition 736, 740 with 741, 742 with 743, 744 with 745 and 746 with 747. The difference lies in the supplier of magnesium as mentioned in Table 3.1.

In addition, a cross check was done with composition 11EM0739 using the EkviCalc code, as well as the NASA CEA thermodynamic code. More background on these codes can also be found in a recent review of these codes (Koch, 2010). All three codes produced comparable results.

4 Work Package 3 – Laboratory-scale tests

The laboratory scale tests have been performed on the sodium chlorate based compositions (Table 3.1) and compared with the conventional Hexachloroethane (HC) smoke composition, Red Phosphorus (RP) smoke composition and a Terephthalic acid (TPA) smoke composition.

The lab-scale tests that were performed are:
- Safety tests friction- and impact-sensitivity
- Smoke transmission test in a smoke-box
- Particle size and particle size distribution
  In vitro toxicity screening tests

4.1 Materials

The composition (Table 4.1) for the HC smoke used in this study is based on the composition described in the literature (Ellern, 1968).

Table 4.1. Hexachloroethane (HC) smoke composition

Ingredient	*Weight percentage*
Zinc oxide (ZnO)	46.5
Hexachloroethane (HC)	44.5
Aluminium (Al)	9.0

The TPA smoke composition (Table 4.2) used in this study is based on a composition described by Collins (Collins, 1998).

Table 4.2. Terephthalic (TPA) smoke composition

Ingredient	*Weight percentage*
Terephthalic acid (TPA)	56.0
Potassium chlorate ($KClO_3$)	23.0
Sugar, powdered	14.0
Magnesium carbonate ($MgCO_3$)	3.0
Stearic acid	3.0
Polyvinyl alcohol (PVA)	1.0

The RP smoke was generated from the ignition of coated red phosphorous. This RP was manufactured by Clariant.

4.2 Safety tests

TNO's obscurant composition is based on a chlorate as an oxidizer. It is well known that chlorates have a bad reputation related to their greater sensitivity to friction and impact in

comparison with nitrates and perchlorates. However, it should be noted that many pyrotechnic compositions can be considered sensitive to friction and impact.

The sensitive nature of pyrotechnic compositions varies depending on many factors, such as the choice for oxidizer, fuel, particle size and mixture ratios. A German BAM report (Trentmann, 1987), also known as the . '*BAM Forschungsbericht 142*' report measured sensitivity data of various chlorate containing pyrotechnic compositions with various mixture ratios. It shows that also other oxidizers, for instance potassium perchlorate has comparable impact sensitivity compared to sodium chlorate. However the friction sensitivity of sodium chlorate is higher, than for the potassium perchlorate.

TNO conducted safety tests on a selection of TNO's sodium chlorate based obscurant compositions (11EM0739, -744, -745 and -746). The safety tests include testing of the compositions on friction (Figure 4.1)- and impact (Figure 4.2)-sensitivity. The friction sensitivity of the compositions was tested according to the UN- guidelines (UN-test 3(b)(i)). The impact sensitivity of the compositions was tested according to the BAM Fallhammer guidelines (UN-test 3(a)(ii)). This is done by, using dry compositions powders. The results are shown in Table 4.3 and Table 4.4.

The conventional HC and TPA smoke compositions are not tested for safety, since these compositions are already a long time in use. Therefore, it is expected that these compositions are relatively insensitive to friction and impact.

Figure 4.1 BAM equipment for testing the friction sensitivity of compositions.

Figure 4.2 BAM equipment for testing the impact sensitivity of compositions.

Table 4.3 Test results of friction sensitivity for the sodium chloride based obscurant compositions.

EM-code	*Friction sensitivity [N]*	*Relative humidity [%]*	*Temperature [^oC]*
11EM0739	84	51.8	18.1
11EM0744	108	48.0	17.8
11EM0745	120	47.1	17.7
11EM0746	84	45.9	18.1

Table 4.4 Test results of impact sensitivity for the sodium chloride based obscurant compositions.

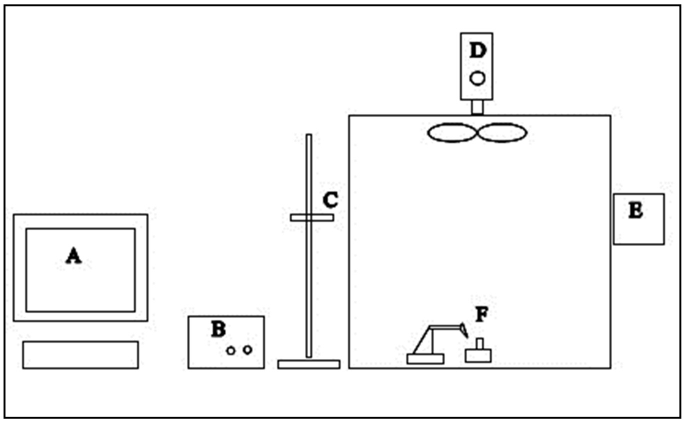
EM-code	*Impact sensitivity [Nm]*	*Relative humidity [%]*	*Temperature [^oC]*
11EM0739	7.5	49.6	20.4
11EM0744	15	54.2	15.5
11EM0745	30	47.0	18.1
11EM0746	15	52.5	16.1

From the friction and impact results (Table 4.3 and Table 4.4) it is concluded that sample 11EM0739 is the most sensitive sample for both friction as for impact from all in this project the measured sodium chloride based compositions. The composition is slightly more sensitive to friction than RDX and HMX (both 120 N). The sensitive to impact is inline with RDX and HMX (both 7.5 Nm).

4.3 Smoke box tests

4.3.1 Experimental setup

In order to quantitatively assess the amount of smoke produced during the combustion of the conventional and alternative smoke compositions, smoke box tests have been performed. In Figure 4.3 the schematic overview and the actual experimental set-up is presented. This smoke box setup has proven to be a straightforward method for the quantification of the formed smoke. The (internal) dimensions of the smoke box are 675×625×605 mm (W×H×D).



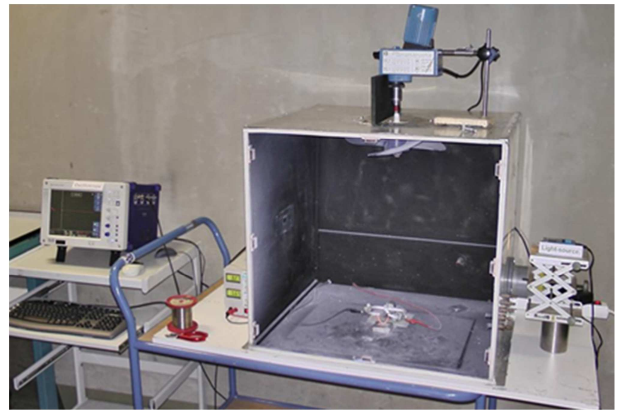


Figure 4.3: (left) Schematic illustration of experimental setup, where A =Computer/Oscilloscope, B = Electric current/ignition source, C = Detector/Sensor, D = Fan, E = Light source and F = Test-sample. (right) photo of the smoke box .

The light source (E), optimized for visual and near-infrared wavelength area 360-2500 nm, (LS-1 Tungsten Halogen light source from Ocean Optics) is placed at a distance of 109 mm from the right side of the smoke box. The light from this light source enters the smoke box through a hole in the right side of the smoke box with a diameter of 6 mm. In this way, the scattering of light in the smoke box is minimized, resulting in a converging bundle of light on the light detector.

The light detector (C) (TAOS TSL250R light-to-voltage optical sensor) is mounted on the exterior wall on the left side of the smoke box, at the same height as the hole in the left side of the smoke box with a diameter of approximately 6 mm. Since the holes in both the left and right sidewalls of the smoke box are situated at the same height, the light from the light source is aligned with light detector. The loss in transmission, caused by the presence of the obscuration smoke in the light path, results in a quantified measure for the smoke formation. The difference between the two reference signal (2 Volts) and the signal measured during the smoke experiment, is a measure for the transparency for smoke produced.

The light detector is connected to an calibrated oscilloscope (A) (Nicolet Sigma 30) in order to continuously monitor the output voltage. The settings are used for the oscilloscope are listed in Appendix A.

The test samples (F), are ignited by a resistance wire (Nickel-Chrome, 0.2 mm diameter from British Driver Harris, UK). This wire is heated by applying a current (Figure 4.4) through the wire applied by a variable electric current source (B).This current is slowly increased to 2 Amperes, at which the wire would start to glow and hence igniting the sample.
To make sure the smoke is homogeneously distributed in the smoke box, a fan (D) is used.

Figure 4.4 Experimental set-up of the smoke box during an experiment.

4.3.2 *Transmission & mass extinction coefficient (Law of Lambert-Beer)*

For the determination of the transmission from the smoke box tests, the Lambert-Beer equation (Eq. 4.1)

$$\tau = \frac{I_\lambda(L)}{I_{\lambda,0}} = \frac{I_{smoke}}{I_{zero}} \tag{4.1}$$

Where;

τ visual transmission of the light through the medium
$I_\lambda(L)$ light intensity after travelling a distance L through the medium
$I_{\lambda,0}$ initial light intensity
I_{smoke} light intensity through the smoke in the box
I_{zero} light intensity in empty (without smoke) box

Since the output voltage of the light sensor is proportional to the intensity of the incoming light, the intensity can be replaced by the output voltage:

$$\tau = \frac{V_{smoke}}{V_{zero}} \tag{4.2}$$

Where;

τ visual transmission of the light through the medium
V_{smoke} photodiode voltage signal after the light passes the smoke in the box
V_{zero} photodiode voltage signal in empty (without smoke) box

However, this equation does not account for a possible offset voltage signal produced by the light sensor, even when no light enters its optics. To account for this addition signal, the

output voltage of the light sensor is measured without the light striking the photosensitive cell. This value has to be subtracted from the measured signals which transforms the equation 4.2 into equation 4.3.

$$\tau = \frac{V_{smoke} - V_{offset}}{V_{zero} - V_{offset}} \tag{4.3}$$

Where;

τ visual transmission of the light through the medium

V_{smoke} photodiode voltage signal after the light passes the smoke in the box

V_{zero} photodiode voltage signal in empty (without smoke) box

V_{offset} background photodiode voltage signal

The transmission determined from the smoke box tests using the previous equation, can be used to determine the (mass) extinction coefficient for the visual part of the spectrum. This can be done by using the following equation:

$$\tau = \frac{I_\lambda(L)}{I_{\lambda,0}} = e^{-\beta \cdot L} \tag{4.4}$$

Where;

τ visual transmission

$I_\lambda(L)$ light intensity after travelling a distance L through the medium

$I_{\lambda,0}$ initial light intensity

L distance light has to travel through the medium; the width of the box

β extinction coefficient or the scattering coefficient ($\beta = \alpha * c$ or $\beta = \alpha * \rho$)

The extinction coefficient or scattering coefficient β [m^{-1}] can be rewritten as $\beta = \alpha * c$ or $\beta = \alpha * \rho$, where α is the mass extinction coefficient [$m^2 * kg^{-1}$], c is the concentration of the smoke [$kg * m^{-3}$], and ρ is the density of the smoke [$kg * m^{-3}$]. Using this in the previous equation gives:

$$\tau = e^{-\alpha \cdot c \cdot L} \tag{4.5}$$

or

$$\tau = e^{-\alpha \cdot \rho \cdot L} \tag{4.6}$$

Where:

τ visual transmission

α mass extinction coefficient

c concentration of the smoke

ρ density of the smoke

L distance light has to travel through the medium; thus the width of the box

With this equation, the mass extinction coefficient of an obscurant is easily calculated from the measured transmission as:

$$\alpha = -\frac{\ln(\tau)}{c \cdot L} \tag{4.7}$$

or

$$\alpha = -\frac{\ln(\tau)}{\rho \cdot L} \tag{4.8}$$

Where;

τ visual transmission
α mass extinction coefficient
c concentration of the smoke
ρ density of the smoke
L distance light has to travel through the medium; thus the width of the box

The equations mentioned above can be summarized as follows:

$$\tau = \frac{I_\lambda(L)}{I_{\lambda,0}} = \frac{I_{smoke}}{I_{zero}} = e^{-\alpha \cdot c \cdot L} \tag{4.9}$$

or

$$\tau = \frac{I_\lambda(L)}{I_{\lambda,0}} = \frac{I_{smoke}}{I_{zero}} = e^{-\alpha \cdot \rho \cdot L} \tag{4.10}$$

4.3.3 Test series

4.3.3.1 Calibration procedure

Prior to the actual test series in the smoke box, preliminary tests have been performed in order to check the alignment of the light source and the light detector, determine the optimal intensity and the optimal amount of smoke composition needed for the smoke box tests.

The preliminary tests with loose powder in the smoke box shows that in some cases significant amounts of unburned material remained in the smoke box after combustion. In order to minimize this incomplete combustion of the smoke compositions, pellets have been produced for all the smoke box test series (except for the RP due to its sensitivity towards friction and impact). The better performing composition from the preliminary tests was 11EM0739, when comparing all the base compositions listed in Table 3.1.

For creating the calibration curve composition 11EM0739 was used (Figure 4.5). Various amounts, between 0.1 and 1.0 gram with increments of 0.1 gram, have been pressed into pellets with a diameter of 10 mm with a pressure of 611 bar in the press mould (100 bar on the pressure gauge). In the next step, the pellets have been tested in the smoke box one by one. The test are performed with an average relative humidity of 34 %, and an average temperature of 21 ^{o}C.

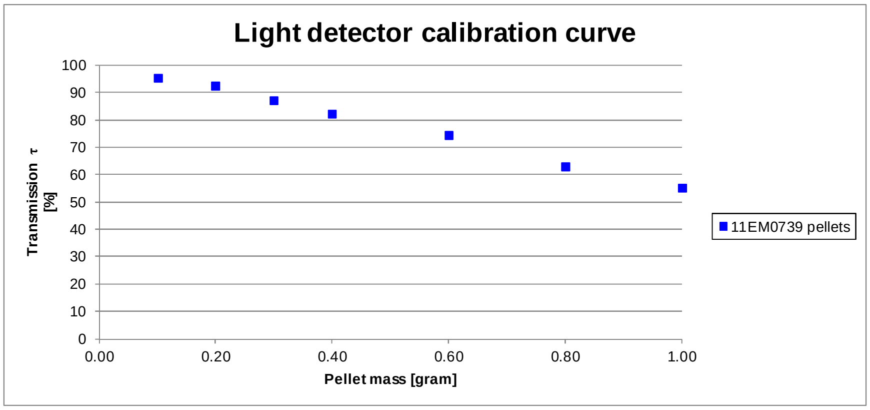


Figure 4.5 Calibration curve obtained for composition 11EM0739.

For the determination of the (final) obscurant compositions the pellet masses for the smoke box tests, it is important that the pellet mass be substantial in order to achieve a significant amount of smoke to decrease the transmission signal. However too much material is also not desirable since pellets of the conventional obscurant compositions (HC, RP and TPA) also need to be tested, giving a representative signal. Considering this, the HC and RP conventional obscurant compositions are tested with 0.3 grams and 0.5 gram of material to make sure it follows a linear trend (Increasing amount gives a linear increase in signal). For this reason the used amount for the experiments is 0.5 gram for all the smoke box experiments.

4.3.3.2 Smoke box tests of conventional smoke compositions (HC, RP, TPA)

All the compositions are tested in triplicate, with the exception of RP and TPA compositions which are tested in respectively onetime and in five-fold. The results of the smoke box experiments are presented in Figure 4.6. The maximum error for these tests is 6 %.

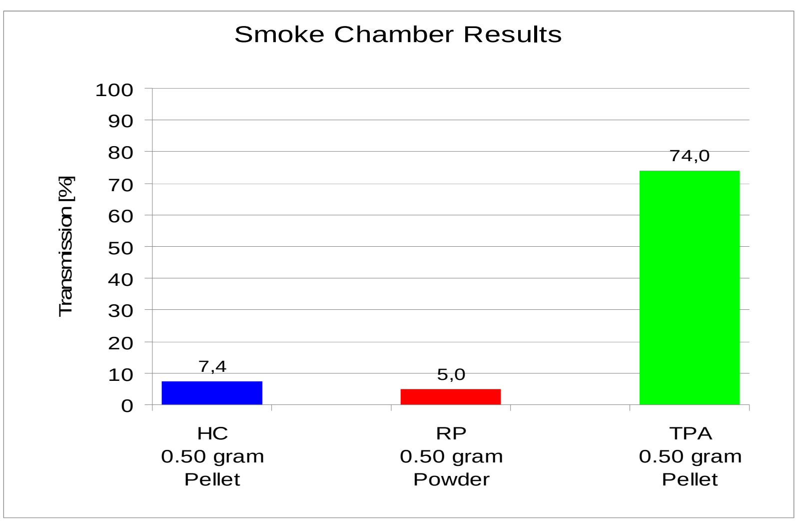


Figure 4.6: Smoke production in terms of transmission for the conventional obscurant compositions hexachloroethane (HC), red phosphorus (RP), and terephthalic acid (TPA).

Figure 4.6 shows that the RP obscurant composition produces the highest obscurancy, while the TPA composition produces the least per 0.5 gram composition.

For the conversion (§ 4.3.2. Equation 4.4) of the transmission to the mass extinction coefficient (α), instead of the whole 360-2500 nm, only the visual wavelengths are taken into account. In Figure 4.7 the mass extinction coefficient for all three conventional obscurant compositions are shown.

In the calculations from transmission to the mass extinction coefficient (α) it is assumed that the pellet mass of 0.50 gram is completely converted into smoke after combustion. This is not completely true because from the smoke box tests with the conventional obscurant compositions it is shown that some residue still remains after combustion. With a full combustion a lower transmission will be accomplished. However, in this feasibility study this assumption is considered to be sufficient enough.

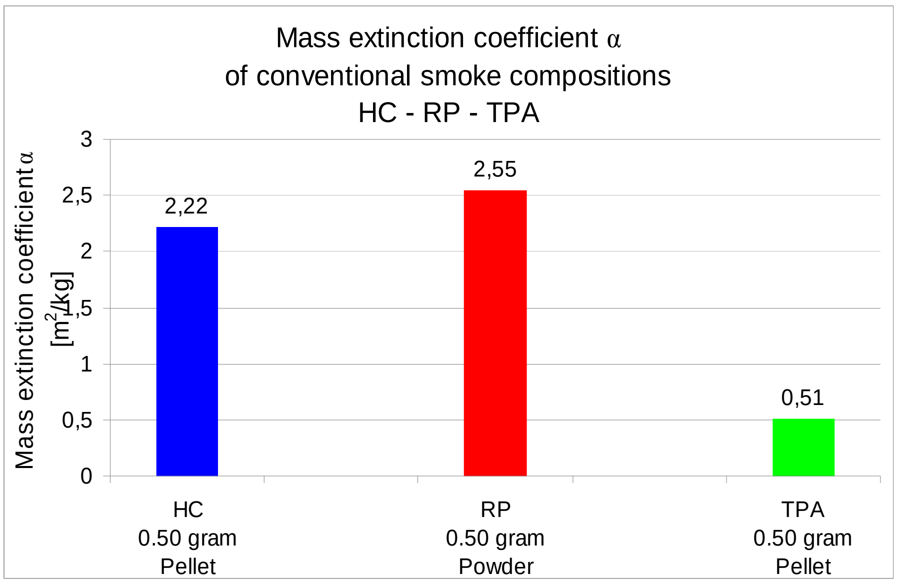


Figure 4.7 Mass extinction coefficients of the conventional obscurant compositions hexachloroethane (HC), red phosphorus (RP) and terephthalic acid (TPA).

The average relative humidity and average temperature measured during these smoke box tests are listed in Table 4.5. Unfortunately the relative humidity and temperature has not been measured for the RP obscurant composition during the smoke box tests

Table 4.5: The average relative humidity and average temperature measured during the smoke box test of hexachloroethane (HC) and terephthalic acid (TPA).

	Relative Humidity [%]	*Temperature [ºC]*
HC	42	23
TPA	30	26

A large difference in the relative humidity is noticeable between the HC smoke box tests and the TPA smoke box tests. Since both compositions are hygroscopic, the test results presented above may alter when these compositions are tested under identical conditions.

4.3.3.3 Smoke box tests of the sodium chloride based smoke compositions

The sodium chloride based smoke compositions (11EM0735 to 11EM0747), have been tested in the smoke box, following the identical procedure (0.5 gram pellets in triplicate) as the conventional obscurant compositions. The average transmission from the triplicate tests are presented in Figure 4.8. The maximum error for these tests is 6 %. The test are performed with an average relative humidity of 35 %, and an average temperature of 23 ^{o}C.

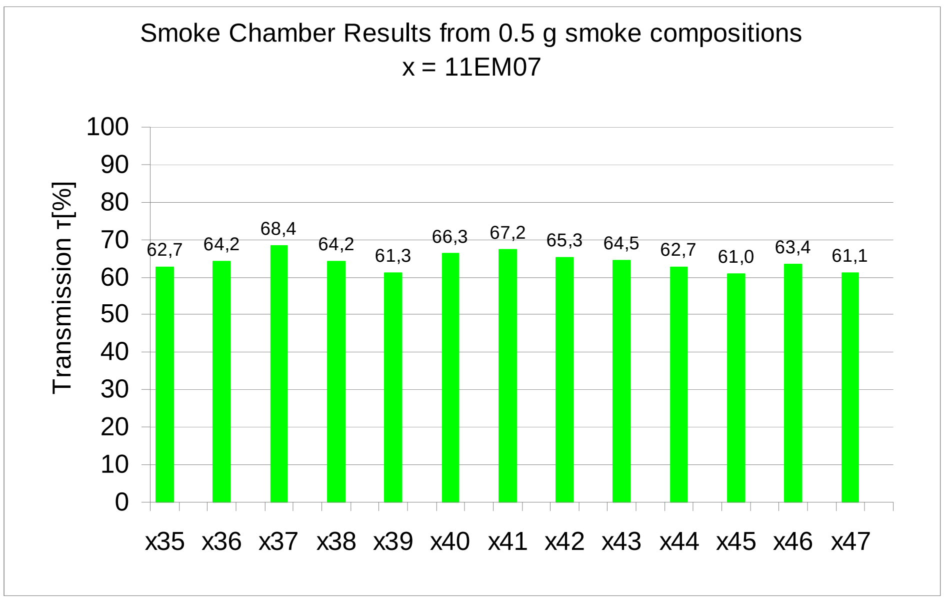


Figure 4.8 Smoke production in terms of transmission for the sodium chloride based obscurant compositions.

Also for here the percentage of transmission is converted (§ 4.3.2. Equation 4.4) to mass extinction coefficient (α) and plotted (Figure 4.9).

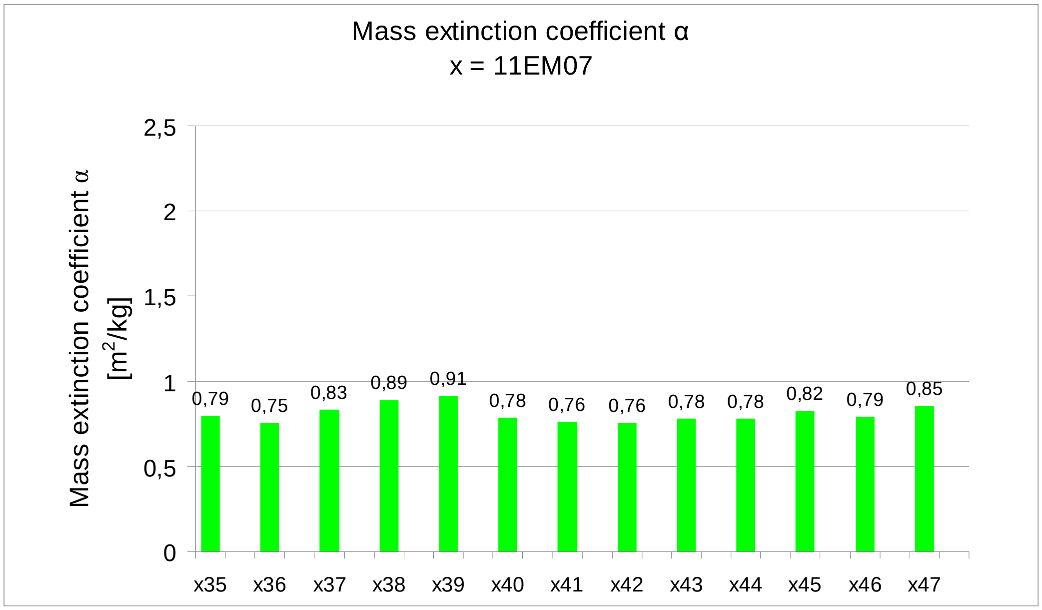


Figure 4.9 Mass extinction coefficients of the sodium chloride based obscurant compositions.

In general the compositions do not show significant differences in transmission (Figure 4.8). The mass extinction coefficients (Figure 4.9) are calculated with percentage solids (Table 3.3). Based on the transmission results, combined with the friction and impact data (§4.2 Table 4.3 and Table 4.4), composition 11EM0745 is chosen as the most optimal composition.

When comparing this sodium chloride based obscurant composition 11EM0745 with the conventional compositions, it is observed that its performance is significantly lower than the performance of the HC and RP smoke compositions. However, the 11EM0745 composition appears to perform better than the conventional TPA smoke composition.

Besides the smoke characteristics, also the ignition behaviour is of importance. The conventional obscurant compositions showed considerable ignition problems and/or ignition delay, whereas virtually no ignition problems have been noticed with the sodium chloride based obscurant compositions.
Furthermore, when comparing the amounts of residue of the conventional and the sodium chloride based obscurant compositions, it has been observed during the smoke box tests that the sodium chloride based obscurant compositions produce far les residue after combustion than the conventional obscurant compositions.

4.4 Particle size and particle size distribution of smoke particles

The determination of the particle size and the particle size distribution is performed by Scanning Electron Microscopy (SEM). The obscurant particles, produced during the combustion of the obscurant compositions, are collected on carbon stubs which has been placed inside the smoke box at a height of approximately 200 mm using a lab jack.

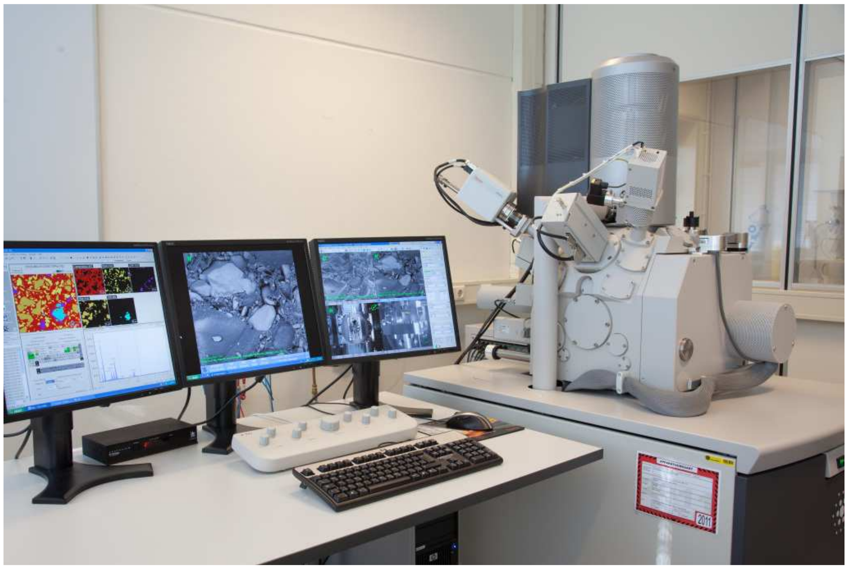


Figure 4.10 FEI Nova NanoSem 650 at TNO

The carbon stubs contain a 3 mm thick carbon sticky layer with a diameter of 12.5 mm. The SEM analyses are performed on a FEI Nova NanoSem 650 SEM apparatus (Figure 4.10), using the following settings:

- Chamber pressure: 20 Pa.
- Detector: Gaseous Analytical Detector (GAD).
- Energy: 5 kV.

The determination of the particles size and particle size have been carried out for the conventional obscurant composition (HC) and for all the sodium chloride based obscurant compositions (11EM0735 to 11EM0747). The SEM-images from the particles collected during the smoke box experiment with the conventional obscurant composition HC are presented in Figure 4.11 and Figure 4.12 for the best performing sodium chlorate based obscurant composition 11EM0745. The SEM-images of other sodium chlorate based compositions are presented in the Appendix B.

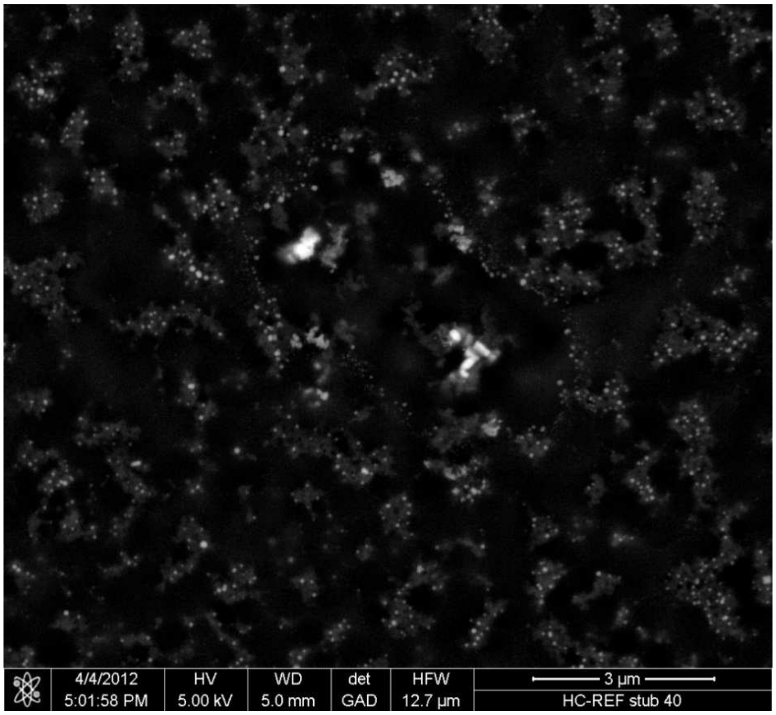


Figure 4.11: SEM image of the conventional obscurant composition HC

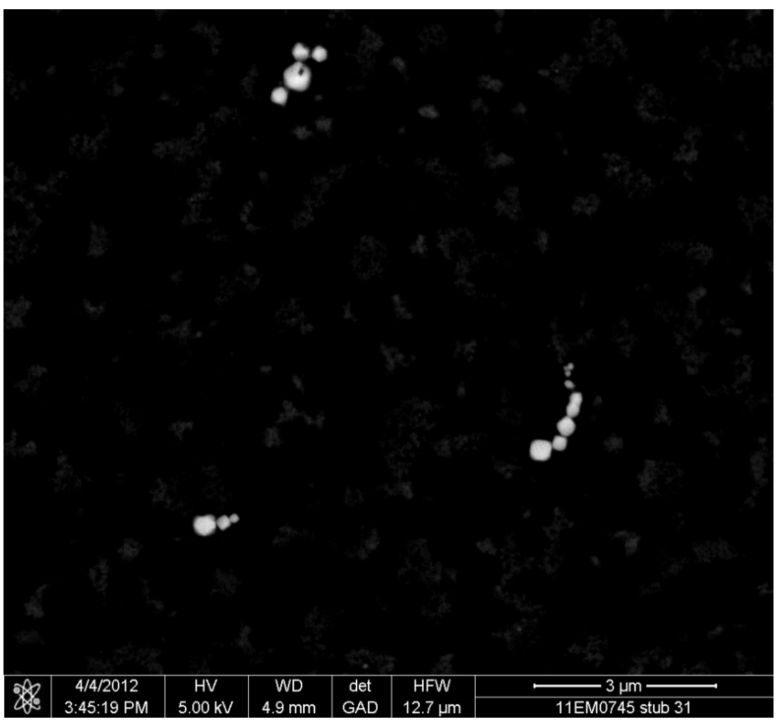


Figure 4.12 SEM image of the sodium chloride based obscurant composition 11EM0745

When comparing these two SEM images, it is noted that the average particle sizes of the smoke particles for the sodium chloride based obscurant composition (11EM0745) are larger than the particle sizes of the smoke particles from the conventional obscurant HC

composition. Particle size analyses is performed on the two samples and plotted (Figure 4.13 and 4.14).

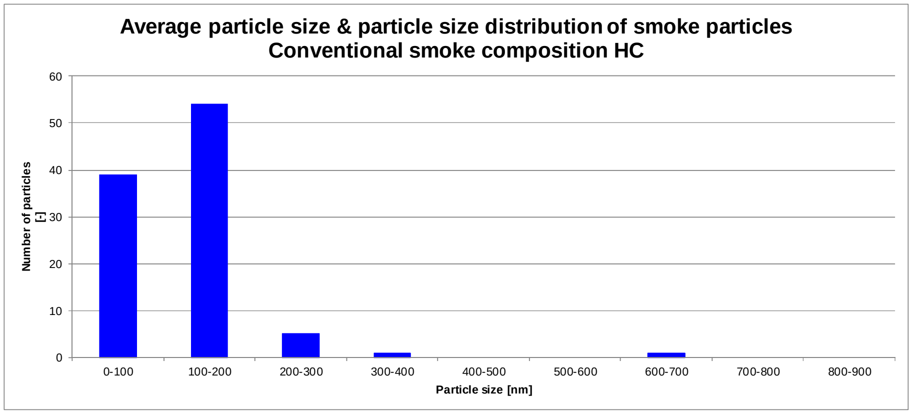


Figure 4.13: Average particle size & particle size distribution of smoke particles for the conventional obscurant composition HC,

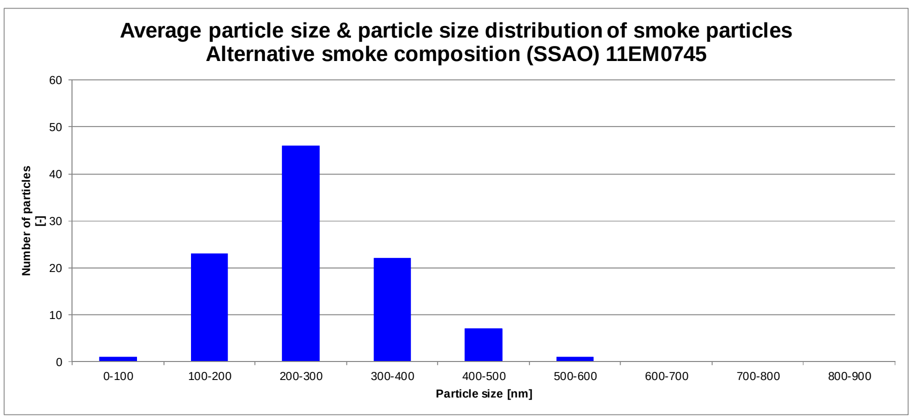


Figure 4.14 Average particle size & particle size distribution of smoke particles for the sodium chloride based obscurant composition 11EM0745

The average particle size and particle size distribution of composition 11EM0739 show similar results compared to the 11EM0745 composition, with a peak average particle size of 200 to 300 nm, and a peak average particle size distribution between 100 and 400 nm.

4.5 In vitro toxicity screening tests of obscurant compositions (CULTEX)

Within the “Statement of Need” a reference was made to ASTM E2552. In ASTM E2552 is a section on approved *in vitro* studies for performing toxicity screening tests. The *in vitro* method used in this project is such an approved test.

For the conventional obscurant compositions HC, RP, and TPA as well as for the alternative obscurant compositions 11EM0739 and 11EM0745 *in vitro* toxicity screening tests have been performed using the CULTEX® system. This system was developed by the Fraunhofer Institutes (Germany) to test toxicity of tobacco smoke and substitutes thereof. CULTEX® is highly suitable to study inhalation toxicity because the system allows exposure of human lung cells in culture via an air-liquid interface, thus mimicking the *in vivo* situation. One of the application of the CULTEX® is descripted by Wijte and colleagues (Wijte et al., 2011)

To assess cell viability, a dye called Alamar Blue is used in the CULTEX® tests. This test is suitable for the purpose as described in ASTM E2552-08. It is also possible to do this test with human lung tumor cells (A549) and human keratinocytes (HaCaT) in culture. Literature seems to suggest that the Alamar Blue test is more sensitive than the MTT-assay mentioned in ASTM E2552-08. (The MTT-assay method is a colorimetric assay for measuring enzyme activity. The abbreviation MTT is derived from the tetrazolium salt 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide used in this method.)

In the CULTEX® tests a Weiss Enet climate chamber was used, with dimensions (W x D x H) 1.52 m x 1.38 m x 1.60 m (total internal volume of 3.36 m^3). For each test of the conventional and alternative obscurant compositions, samples of 10.0 gram powder have been used. Each test has been carried out in duplicate. The exposure times of the cells to the smoke was 2 and 15 minutes. The biomarkers Alamar Blue and LDH have been used in the tests.

The Alamar Blue assay is a biomarker for mitochondrial activity of cells. The mitochondrial activity can be determined by adding a non-toxic dye called Alamar Blue (contains Resazurin) to the medium in which the cells are cultured after exposure. The blue chemical is transferred to resorufin (red fluorescent) by cell activity. Only living cells transfer resazurin to resorufin, which increases the fluorescence of the medium. This increase is measured according to manufacturers instructions (Invitrogen).

Lactate DeHydrogenase (LDH) catalyses the reversible oxidation of lactate to pyruvate. When a cell dies, LDH is released into the medium. This release is measured with an LDH assay according to manufacturers instructions (Roche, Mannheim, Germany). The optical density was measured at a wavelength of 450 nm with a micro plate reader µQuant (BioTek Germany, Bad Friedrichshall, Germany).

Similar to the smoke box tests, the obscurant compositions have been ignited using the same resistance wire (Nickel-Chrome from British Driver Harris). This wire was again heated by applying a current through the wire. An impression of the CULTEX® tests with the smoke formulations is illustrated in Figure 4.15 to 4.18.

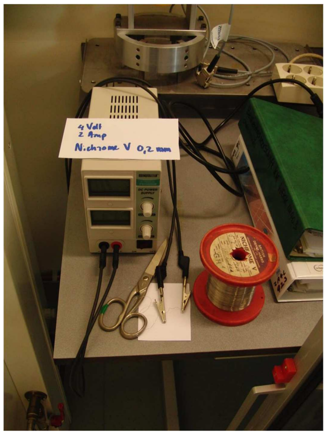


Figure 4.15 The variable electric current source and the resistance wire (Nickel-Chrome, 0.2 mm diameter from British Driver Harris, UK) used for both the smoke box tests and the CULTEX® tests.

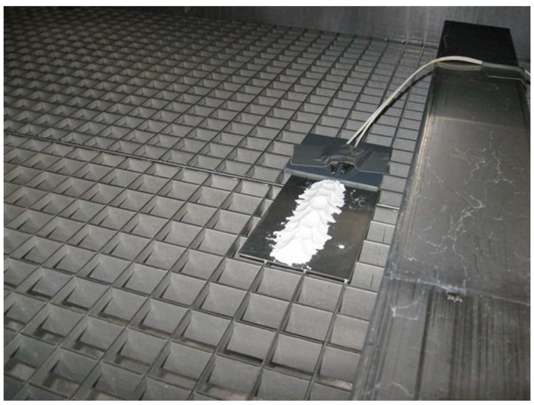


Figure 4.16 The obscurant composition placed on a metal plate inside the Weiss Enet climate chamber prior to ignition by the resistance wire, which is connected to the variable electric current source.

Figure 4.17 Ignition of the obscurant composition within the Weiss Enet climate chamber for the CULTEX® tests.

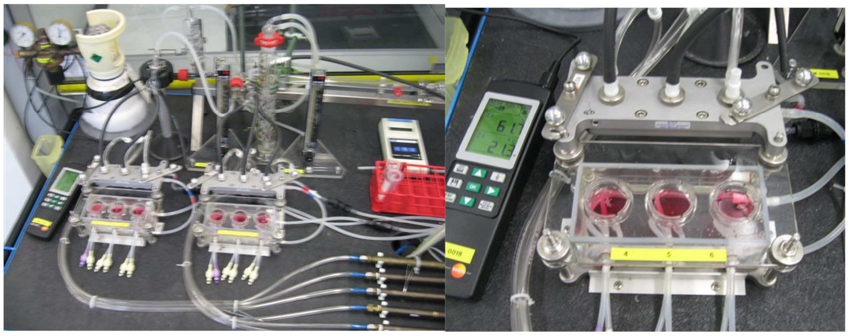


Figure 4.18 The CULTEX® system (left) and a close-up of the human epithelial lung cells in vitro in three chambers.

The results of the CULTEX® experiments are presented in Table 4.6 and Figure 4.19 to Figure 4.23. Table 4.6 shows the average relative humidity and the average temperature at which the experiments have been conducted.
On the Y-axis of the graphs the % decrease in cell viability in comparison with control cells (exposed to medicinal air under the same conditions as used for the smoke formulations) is shown for Alamar Blue as a read-out parameter. For LDH as a read-out parameter, the effect is expressed as % increase of the release of LDH in comparison with the control cells.

Table 4.6 The average relative humidity and the average temperature at which the CULTEX® tests have been performed.

Measurement [-]	Exposure time [min]	Relative humidity [%]	Temperature [°C]
HC	2	57.3	22.2
HC	15	58.9	22.3
TPA	2	72.1	21.7
TPA	15	69.9	22.0
11EM0739	2	62.0	21.3
11EM0739	15	62.0	21.3
11EM0745	2	54.9	21.4
11EM0745	15	55.9	21.3

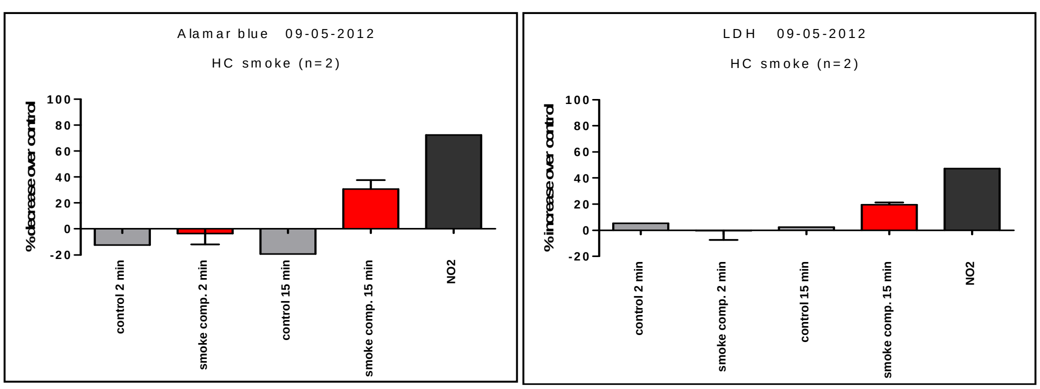


Figure 4.19 CULTEX® test results of the conventional obscurant composition HC for the biomarkers Alamar Blue (left) and LDH (right).

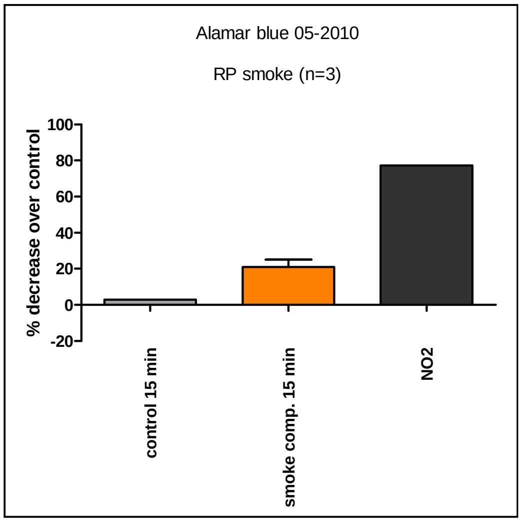
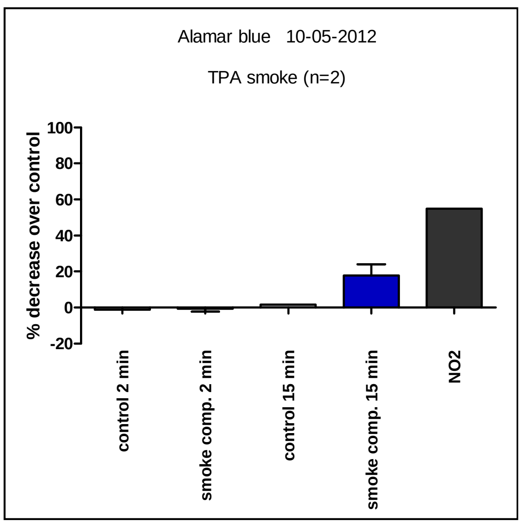


Figure 4.20 CULTEX® test results of the conventional obscurant composition RP for the biomarker Alamar Blue.



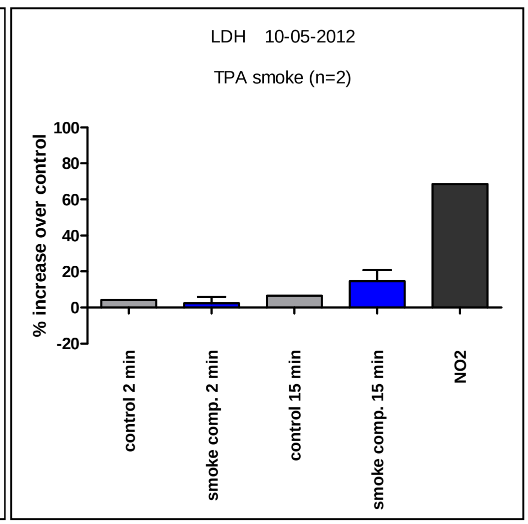


Figure 4.21 CULTEX® test results of the conventional obscurant composition TPA for the biomarkers Alamar Blue (left) and LDH (right).

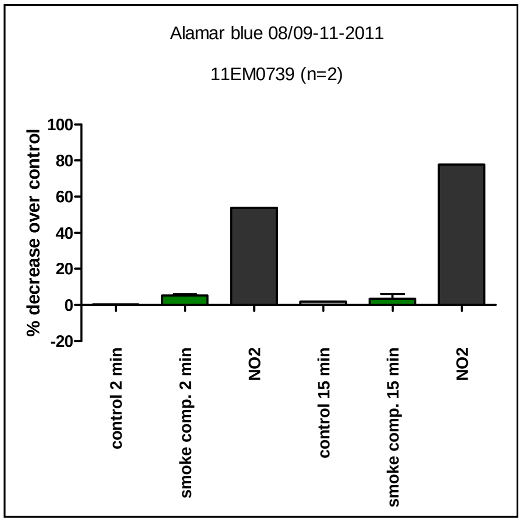
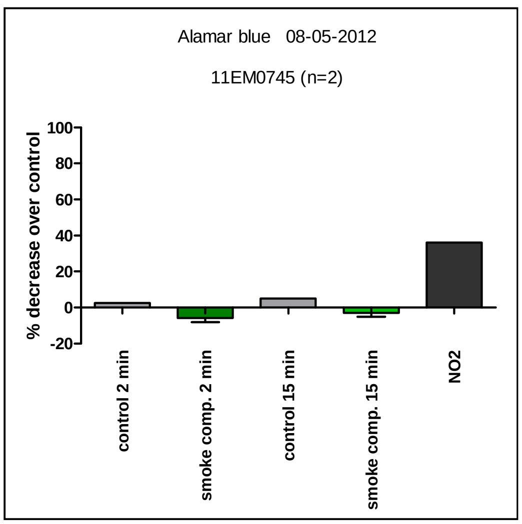


Figure 4.22 CULTEX® test results of the sodium chloride based obscurant composition 11EM0739 for the biomarker Alamar Blue.



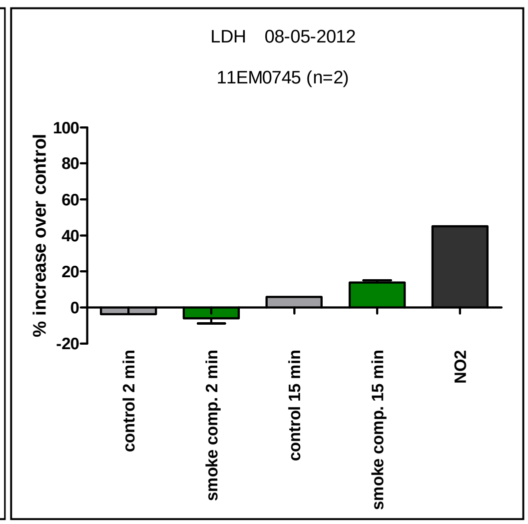


Figure 4.23 CULTEX® test results of the sodium chloride based obscurant composition 11EM0745 for the biomarkers Alamar Blue (left) and LDH (right).

With the CULTEX® system it is very difficult to establish the absolute intrinsic toxicity of an individual compound, or a mixture of compounds. However, the procedure is highly suitable for comparing the intrinsic toxicity of various individual compounds or a mixture of compounds, as has been done in the tests presented above.

In the figures presented above, the positive control (NO_2) shows a clear response in all experiments, both with the Alamar Blue and LDH biomarkers, indicating that the test set-up of the CULTEX® system and the test procedure have functioned according to specification. Similarly, the other (zero) control tests (the clean Weiss Enet climate chamber with respect to medical air) resulted only in a minor positive, or even a negative response.

Observing the test results shown in Figure 4.19 to Figure 4.23, the conventional obscurant composition HC appears to be the most toxic of the obscurant compositions studied. In view of literature data and previous experiences with this obscurant composition, this is to be expected.
The conventional obscurant composition TPA seems to be somewhat less toxic than the HC composition. In addition, the conventional obscurant composition TPA is comparable to the RP composition in terms of toxicity for the Alamar Blue biomarker.
The alternative obscurant composition 11EM0745 shows even less toxicity than the TPA composition. Furthermore, the 11EM0739 composition appears to be somewhat more toxic than the 11EM0745 composition.

It should be noted that the amount of data is too small to support the observations mentioned above with statistical significance. In addition, it is difficult to compare the CULTEX® test results obtained in various time periods, see Figure 4.19 to Figure 4.23. This is caused by variations in the growth of the human epithelial lung cell cultures. Hence, for a proper comparison of the toxicity, it recommended to test all the obscurant compositions within one series of experiments.

5 Work Package 04 – Proof of concept

A downsized version of a obscurant hand grenade has been made, using the TNO composition 11EM0739. For comparison, another exact same size obscurant hand grenade has been made using the HC smoke composition. The latter has been made for reference purposes. Both grenades have been charged with 40 grams of composition. The relative humidity was 54.5%, and the ambient temperature was 25 ^{o}C. (Measured with Testo 625)

The performance of this obscurant grenade was put on two digital videos. These videos will be accompanying this report.

The burn time of the TNO smoke grenade was approximately 16 seconds, whereas the HC smoke grenade was approximately 21 seconds.

The results clearly showed also on this scale that the HC smoke creates a very dense cloud of smoke, whereas TNO's alternative smoke is much thinner. (Figure 5.1)

Figure 5.1 Downsized HC smoke grenade (left) vs TNO's smoke grenade (right)

Examining the TNO smoke grenade hardware afterwards, it was observed that there was still a lot of white (sodium chloride) based combustion residue on the nozzle plate. (Figure 5.2) This indicates that the formation of large particles during the trial, diminishing the effectiveness of the downsized hand-grenade. A better nozzle, as proposed as an improvement, will disperse the combustion products more effective, resulting in a denser aerosol.

Figure 5.2 Residue of salt on TNO’s smoke grenade

6 Conclusions & Recommendations

The composition made contained various amounts of $NaClO_3$, Cellulose, $CaCO_3$ and Mg (from two different sources). From the laboratory scaled tests the composition named “11EM0745” was are the best performing composition made. When these compositions are compared to the benchmark obscurant compositions (HC smoke, red phosphorus smoke, and TPA smoke) it is concluded that the transmissions through the sea-salt compositions are much higher compared to the HC and RP smoke, but lower compared to the TPA smoke. The smoke from developed compositions are less toxic than the HC, RP and TPA smokes. Furthermore the ingredients used are easy to obtain and low in costs.

Recomm 1: *To further enhance the sea salt based obscurant and to continue the search for additional materials capable of efficiently absorb atmospheric moisture and having a low toxicity profile.*

The *in vitro toxicity* screening results suggest that this TNO obscurant composition, derived from sea salt, has a low intrinsic toxicity, in comparison with other, already existing obscurants.
We wish to stress here that the intrinsic toxicity is not the only parameter that determines the potential health hazard to man. For compounds that are mainly inhaled, the particle size distribution is also very important, because relatively low toxic materials may cause serious health problems if they are able to penetrate deep into the respiratory tract. In addition the exposure conditions (concentration of the smoke, duration of the exposure, repeated exposures, heat and humidity, exercising, lifestyle, underlying diseases, etc.) will also determine whether or not the newly designed smoke formulation(s) can pose a health hazard to the soldier.

Recomm 2: *Performing a limited in vivo inhalation toxicity study in rats should be considered as a validation of the in vitro toxicity screening results.*

Scaling effects are expected to work in favour of efficient generation of aerosols. The density of the smoke is influenced by the size of the system (grenade) in which the composition is ignited. Positive effects are expected from the factors like heat losses, gas flow, effects by nozzles, etc.

Recomm 3: *To perform assessment trials on a larger scale, preferably leading towards a comparison of several “full up items”.*

A number of generic “base compositions” have been created that allow the pyrotechnic generation of an aerosol that resembles sea-salt aerosol. A series of compositions has been tested in a smoke box and the transmission was measured. The mass-extinction coefficient was also determined, but this was using calculated values of the probable concentration. To get an optimal composition, working under different atmospheric conditions, the influence of the humidity is an important parameter.

Recomm 4: *An assessment on the effectiveness on a larger scale, preferably use a climate chamber and other relevant obscurants, to compare results. In this same assessment the final composition will be investigated at several levels of humidity from low to high.*

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Appendix A: Setting of the oscilloscope

- Vertical scale:
    - 500 mV/division.
    - 8 divisions.
    - Total vertical scale: 4000 mV (4.0 V).
    - Offset: - 1.3880 V.

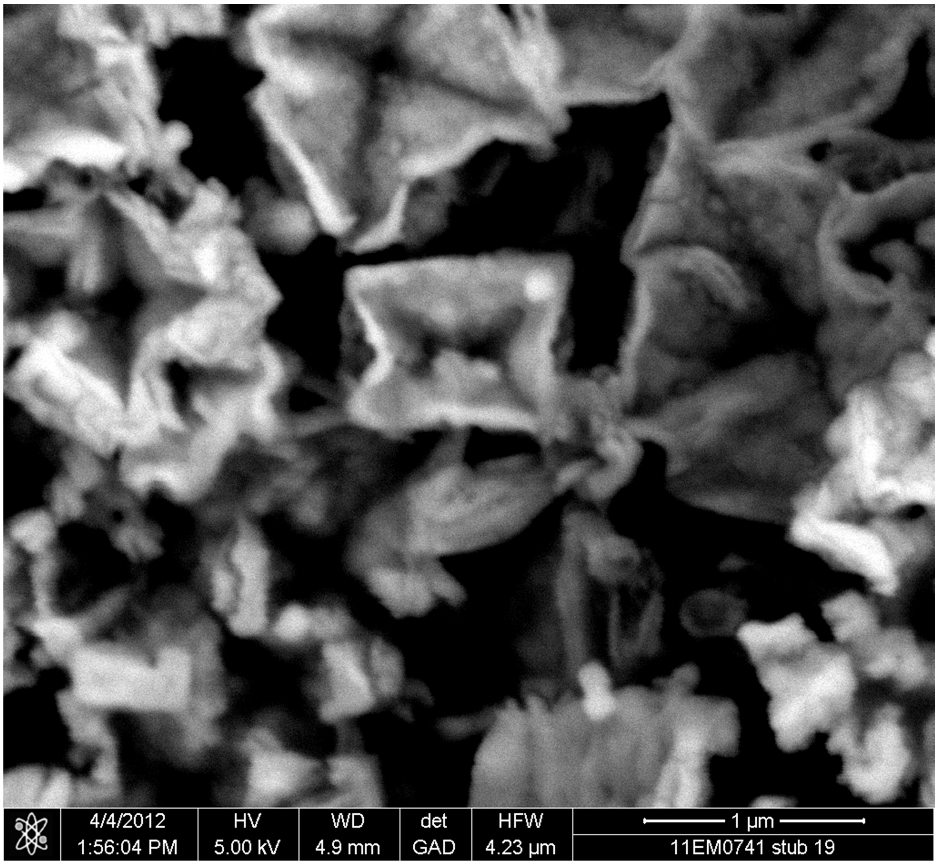
- Horizontal scale:
    - 6 seconds/division.
    - 10 divisions.
    - Total horizontal scale: 60 seconds.
    - Offset: - 6.0 seconds

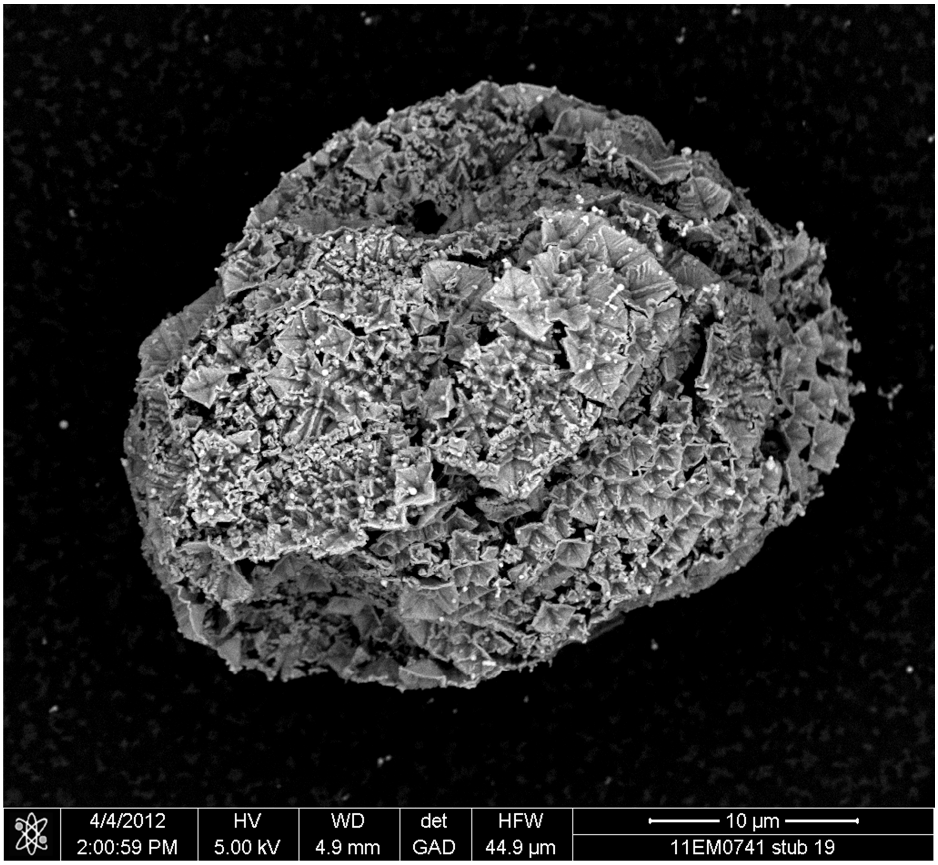
- Data points:
    - 100 data points/second.
    - Total horizontal scale: 60 seconds.
    - Total amount of data points: 6000 data points.

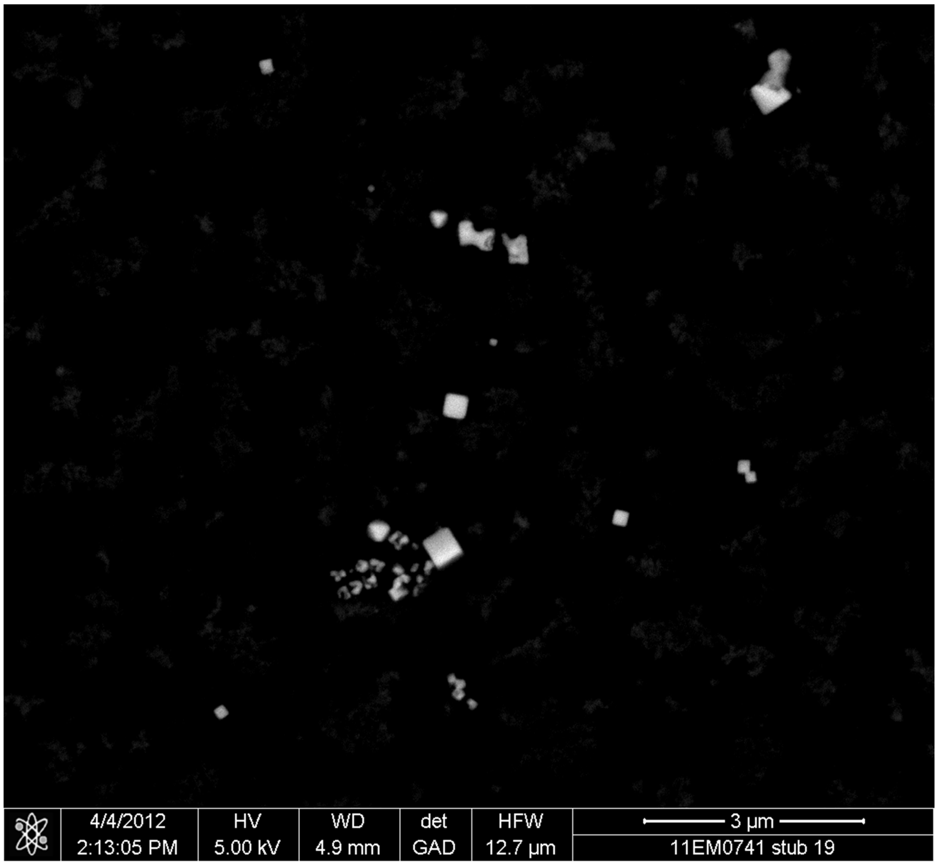
- Trigger:
    - Trigger mode: edge.
    - Trigger slope: negative.
    - Position pre-trigger: 10 %.
    - Trigger level: 2.1265 V.

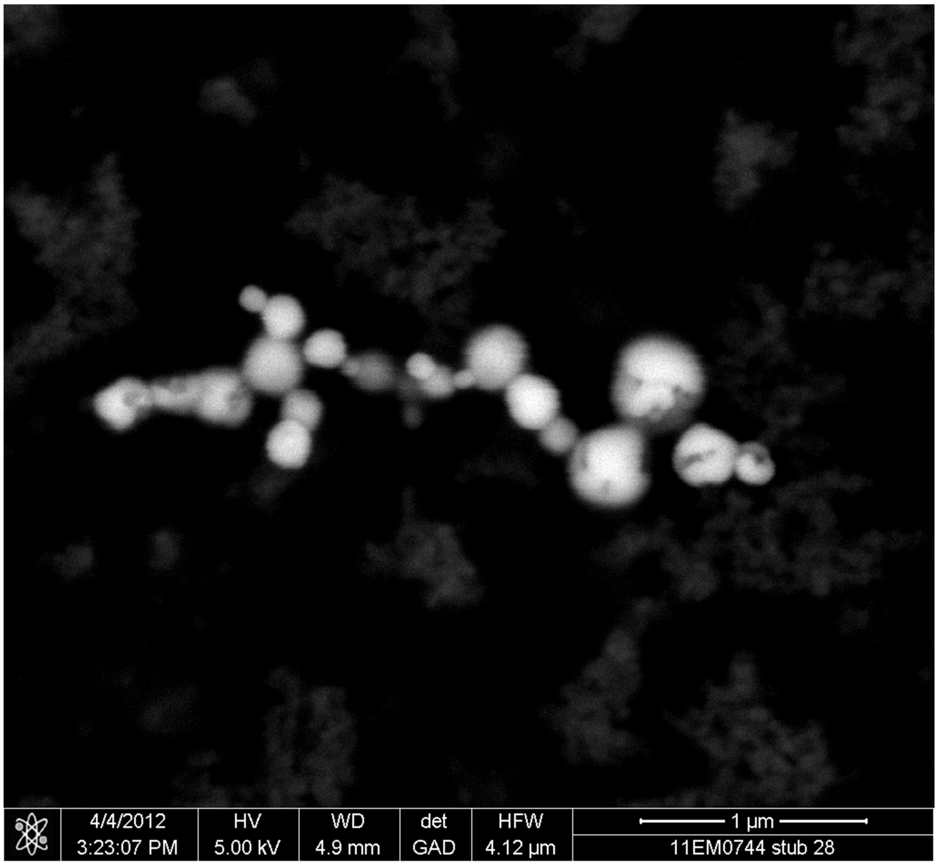
Appendix B: Scanning Electron Microscope Images

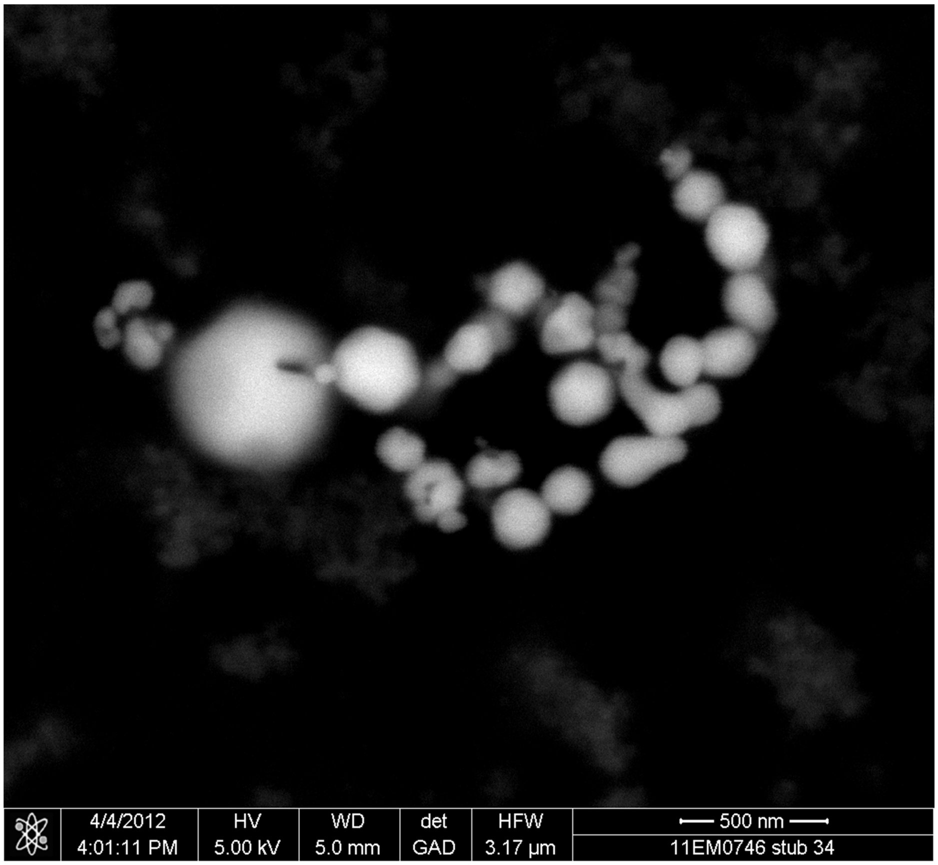
Each image has the sample reference code in the lower right corner.


4/4/2012
1:56:04 PM
HV
5.00 kV
WD
4.9 mm
det
GAD
HFW
4.23 µm
1 µm
11EM0741 stub 19


4/4/2012
2:00:59 PM
HV
5.00 kV
WD
4.9 mm
det
GAD
HFW
44.9 µm
10 µm
11EM0741 stub 19


4/4/2012
2:13:05 PM
HV
5.00 kV
WD
4.9 mm
det
GAD
HFW
12.7 µm
3 µm
11EM0741 stub 19


4/4/2012
3:23:07 PM
HV
5.00 kV
WD
4.9 mm
det
GAD
HFW
4.12 µm
1 µm
11EM0744 stub 28



4/4/2012
4:01:11 PM
HV
5.00 kV
WD
5.0 mm
det
GAD
HFW
3.17 µm
500 nm
11EM0746 stub 34